(12)

OFFICE OF NAVAL RESEARCH

(15) Contract N00014-78-0015 F

Task No. NR 356-522

(14) TR-7

(9) Technical Report #7

(6) PIEZO- AND PYROELECTRICITY OF POLY(VINYLIDENE FLUORIDE) FROM PLASMA POLING

by

(10) John E. McKinney and G. Thomas Davis

Prepared for Publication in

ACS Polymer Preprints

(11) 1 Dec 77

(12) 11 p.

National Bureau of Standards
Bulk Properties Section
Washington, D. C. 20234

December 1, 1977

DDC
RECEIVED
JAN 23 1978
B

240 800

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report #7	**2. GOVT ACCESSION NO.**	**3. RECIPIENT'S CATALOG NUMBER**
4. TITLE (and Subtitle) "Piezo- and Pyroelectricity of Poly(Vinylidene Fluoride) from Plasma Poling"		**5. TYPE OF REPORT & PERIOD COVER:** Technical Report #7
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) John E. McKinney and G. T. Davis		**8. CONTRACT OR GRANT NUMBER(s)** N00014-78-0015 F
9. PERFORMING ORGANIZATION NAME AND ADDRESS National Bureau of Standards Bulk Properties Section, Polymers Division Washington, D.C. 20234		**10. PROGRAM ELEMENT, PROJECT, TA: AREA & WORK UNIT NUMBERS** NR 356-522
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Chemistry Program Office Arlington, Va. 22217		**12. REPORT DATE** December 1, 1977
		13. NUMBER OF PAGES 18
14. MONITORING AGENCY NAME & ADDRESS(If different from Controlling Office)		**15. SECURITY CLASS. (of this report)** Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

According to the attached distribution list.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, If different from Report)

18. SUPPLEMENTARY NOTES

To be published in ACS Polymer Preprints

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Dielectric; piezoelectric; plasma; polarization; poling; poly(vinylidene fluoride); pyroelectric

ALPHA
BETA

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A plasma poling device is described which allows essentially instantaneous poling of polymeric films at room temperature at very high fields. Using poly(vinylidene fluoride) both undrawn (comprising essentially pure α conformation) and biaxially drawn (both α and β conformation) were polarized in this manner. The polarization of the sample was determined from current integration measurements. The piezoelectric and pyroelectric coefficients were then measured and compared with those estimated from the polarization

DD FORM 1 JAN 73 **1473** EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601 |

20.

theory of Mopsik and Broadhurst, which expresses these coefficients as linear functions of polarization. The theory gives an accurate representation of the piezoelectric coefficients, but underestimates the pyroelectric coefficients considerably.

In addition, x-ray measurements from various techniques were made on both drawn and undrawn PVDF samples. For the unpoled samples the results are in good agreement with those in the literature. Some changes in spacings and intensities were observed with poling for both the drawn and undrawn samples. As yet we do not have a clear interpretation of these results in terms of crystal structure changes resulting from polarization.

ACCESSION for

NTIS	White Section	☑
DDC	Buff Section	☐
UNANNOUNCED		☐
JUSTIFICATION		

BY
DISTRIBUTION/AVAILABILITY CODES

Dist.	AVAIL. and/or SPECIAL	
A		

Piezo- and Pyroelectricity of
Poly(vinylidene fluoride) from Plasma Poling

J. E. McKinney and G. T. Davis

Abstract

A plasma poling device is described which allows essentially instant-
aneous poling of polymeric films at room temperature at very high fields.
Using poly(vinylidene fluoride) both undrawn (comprising essentially pure
α conformation) and biaxially drawn (both α and β conformation) were polarized
in this manner. The polarization of the sample was determined from current
integration measurements. The piezoelectric and pyroelectric coefficients
were then measured and compared with those estimated from the polarization
theory of Mopsik and Broadhurst, which expresses these coefficients as linear
functions of polarization. The theory gives an accurate representation of the
piezoelectric coefficients, but underestimates the pyroelectric coefficients
considerably.

In addition, x-ray measurements from various techniques were made on both
drawn and undrawn PVDF samples. For the unpoled samples the results are in good
agreement with those in the literature. Some changes in spacings and intensities
were observed with poling for both the drawn and undrawn samples. As yet we do not
have a clear interpretation of these results in terms of crystal structure changes
resulting from polarization.

<div align="center">

PIEZO- AND PYROELECTRICITY OF
POLY(VINYLIDENE FLUORIDE) FROM PLASMA POLING

By

</div>

<div align="center">

J. E. McKinney and G. T. Davis
National Bureau of Standards
Washington, D.C. 20234

</div>

I. Introduction

This paper is a preliminary report which includes a description of the plasma poling process, the consequences of this kind of poling in terms of piezo- and pyroelectric response, and an attempt to interpret the results in terms of molecular structure.

Conventional poling procedure involves heating the polymer sample to an elevated temperature, applying an electric field for a brief period of time, and then cooling to room temperature under the field. Recently, Southgate[1] has demonstrated that by applying corona discharge at high potential in the vicinity of a poly(vinylidene fluoride) (PVDF) sample, with the opposite side at ground potential, the poling process is essentially completed in several seconds at room temperature. There is also the advantage that higher fields may be obtained by corona or plasma poling. Since poling times are so short it is relatively easy to measure the total charge on the sample from poling, as demonstrated by Southgate. After the applied field is removed, the residual charge is a measure of the irreversible or "permanent" polarization from which it is possible to derive expressions for the piezo- and pyroelectric responses.

The piezoelectric and pyroelectric response from polymers has been related to polarization, which is linear with applied field for amorphous polymers[2]. Since the charge has been measured during the poling process in our work, these data give us the opportunity to evaluate the theory in terms of experimental quantities for semicrystalline polymers as well. It will be shown that the model predicts the piezoelectric response within experimental accuracy; however, some refinement appears to be necessary for the pyroelectric response. On the other hand, some of the experimental values of quantities appearing in the theory are somewhat dubious, it is not appropriate to pass judgement at this time.

There has been considerable recent interest and some speculation on the nature of apparent phase transitions in PVDF resulting from poling at high fields. For example, such behavior is indicated by changes in infrared spectra as observed by Southgate[1]. We are presently conducting investigations along these lines employing various X-ray and IR-techniques.

II. Theoretical Relationships between Piezo- and Pyroelectric Coefficients and Polarization

Using an Onsager type reaction field model, Mopsik and Broadhurst[2] have derived the relation for the polarization

$$P = (\epsilon_{\infty} + 2)(N\mu_0/3V) <\cos \theta> \qquad (1)$$

where ϵ_{∞} is the limiting high frequency dielectric constant of the medium, N is the number of dipole moments each of strength μ_0 in total volume V, and $<\cos \theta>$ is the average cosine of the dipole orientation angle θ. The above relation gives the permanent polarization in a homogeneous, non-conducting, polarizable medium.

With semicrystalline polymers some modification is necessary to take into account the fact that polarization exists only within the crystalline region and the amorphous regions can be slightly conductive. Although the conductivity of poly(vinylidene fluoride) is very small, a gradual decay of polarization results from migration of real charge through the amorphous regions to the crystal surfaces[3].

In order to adapt the continuum model[2] to a semicrystalline medium we assume[4]

$$P = x \frac{3\epsilon_s}{2\epsilon_s + \epsilon_c} P_c \qquad (2)$$

where x is the crystalline fraction based on volume, P_c is the total polarization of the crystalline region, and ϵ is the relative permittivity with subscripts s and c pertaining to sample and crystal respectively. The dipole moments in the amorphous region are assumed to be randomized at temperatures above T_g after removal of the external poling field. To account for the real charge redistribution mentioned above, we include an additional term in eq.(1) which becomes

$$P(t) = x \frac{3\epsilon_s}{2\epsilon_s + \epsilon_c} \left[\frac{N\mu_0}{3} \frac{\epsilon_c + 2}{V_c} <\cos \theta> - \frac{Q'(t)}{A_c} \right] \qquad (3)$$

A_c is the total area of the crystals, and Q' is a time dependent charge at the crystal surfaces which satisfies the boundary conditions

$$Q'(0) = 0 \text{ and } \lim_{t\to\infty} P(t) = 0$$

From application of the experimental definitions

$$d_p = (1/A) [\partial(AP)/\partial p)]_T \qquad (4a)$$

$$\kappa = -(1/A) [\partial(AP)/\partial T]_p \qquad (4b)$$

where d_p is the hydrostatic piezoelectric coefficient, κ is the pyroelectric coefficient, A is the electrode area, and T and p are the temperature and pressure. The final expressions become

$$d_p = P_0\beta_c \left[\frac{2\epsilon_c + 1}{6} + \phi \frac{J_1(\phi)}{J_0(\phi)} \nu \right] \qquad (5a)$$

$$\kappa = P_0\alpha_c \left[\frac{2\epsilon_c + 1}{6} + \phi \frac{J_1(\phi)}{J_0(\phi)} (\nu + \frac{1}{2T\alpha_c}) \right] \qquad (5b)$$

where P_0 is the initial value of $P(t)$ after poling, β_c and α_c are the crystal compressibility and thermal expansion, ϕ is the dipole fluctuation angle, ν is the Gruneisen constant, and J_0 and J_1 are Bessel functions of first kind of order 0 and 1, respectively.

More explicit detail of the development of eqs.(5) will be included in a later publication. In brief, it is assumed that the c cell dimension (along the chain axis) change with temperature or pressure is negligible. Pressure and temperature dependence in ϵ_c are taken from the Clausius Mossotti equation. Considerable simplification in the expressions for d_p and κ ensues from evaluating these quantities at the ultimate polarization $[P(t) = 0]$ when crystal polarization is compensated by real charge at the crystal liquid interface.

III. Experimental

A. Apparatus

The plasma chamber used to generate plasma for the poling process was adapted from a commercial plasma cleaner. The electrode assembly is shown schematically in Fig. 1. An aluminum electrode of 2.5 cm diameter is evaporated on one side of each polymer film sample. The sample is clamped as shown with the bare side exposed to the plasma. The chamber (containing air) is evacuated to and maintained at about 200 mT during the poling process. Water vapor and other condensable gases are removed with a liquid nitrogen trap.

Voltages up to 10 kV may be applied. The corresponding charge transfer is measured with a charge amplifier in series with the high voltage circuit. Electrical leakage was found to be negligible over the short poling times used. From the charge transfer the polarization of the sample was determined.

After poling, a graphite electrode was painted on the bare side of each sample. The electrodes were shorted and the samples stored for at least twelve hours for surface charges to dissipate. The piezoelectric coefficients were then measured using a pressure cell[5] imposing nearly constant rate of pressure change. From the slopes of the pressure-time curves and corresponding currents, d_p is determined. In an analogous manner the pyroelectric coefficient κ is determined from the measurement of current resulting from nearly constant rate of temperature change.

X-ray measurements were made with an automatic scanning diffractometer and a powder camera using Nickel-filtered-Cu $K\alpha$ radiation in both cases. For the powder camera, the sample film was cut into thin strips with dimensions approximately 3 x 0.3 x .025 mm. These were inserted and sealed in a capillary of 0.3 mm diameter.

B. Samples

Two kinds of commercial PVDF semicrystalline samples were studied. The first is a biaxially stretched (blow molded) film for which the polymer chains tend to orient in the plane of stretch. The stretch process converts a portion of the non-polar α (TGTG' conformation) phase to the polar β (planar zig-zag) phase. The second sample is undrawn and contains essentially only the α phase. Both kinds of film are about 25 µm in thickness.

IV. Results and Discussion

Fig. 2 gives the initial polarization P_0 (as measured from the charge remaining after the applied field is removed) plotted against the applied field, or applied voltage, for the biaxially drawn sample. About three seconds are required to reach 90% of the ultimate value of charge at room temperature. As indicated, the data are somewhat erratic. Subsequent hysteresis loops, however, reveal smooth responses with applied field.

In all cases, except the one indicated by the triangle where the field was reversed, the plasma was at negative potential with respect to the electrode. As seen from the figure, there is essentially no polarization below one MV/cm. There is no indication of saturation in the polarization and dielectric breakdown prevents attaining fields much above 3.5 MV/cm. The numbers on the data points indicate correspondence to those on figures which follow.

According to the theory, for which the results are given in eqs.(5), the piezo- and pyroelectric coefficients are linear functions of the initial polarization P_0. The experimental values applied to these equations are given in Table 1. Values of α_c and β_c have been taken for the α (non-polar) phase since these quantities for the β (polar) phase are apparently not available in the literature. The value of α_c was obtained from the expansions of the unit cell dimensions[6]. The value of β_c was estimated by somewhat devious means from macroscopic compressibility measurements of a 68% crystalline fraction sample[7].

In Fig. 3 the piezoelectric coefficient d_p is plotted against the initial polarization P_0. The straight line is a plot of the equation

$$d_p = 2.11 \times 10^{-10} P_0 \qquad \text{(SI units)}$$

which is evaluated from eq.(5a) taking the values given in Table I. In this case the agreement between theory and experiment are essentially within data scatter.

The corresponding pyroelectric response is shown in Fig. 4. The straight line represents the equation

$$\kappa = 2.97 \times 10^{-4} P_0 \qquad \text{(SI units)}$$

evaluated from eq.(5b) again using the experimental values from Table I. There is considerable underestimation by the theory for which the ratio, theoretical/experimental, is about 2/3. At this time we do not know why κ is underestimated.

We also polarized an undrawn PVDF sample composed of the "non-polar" α phase. At an applied field of 1.75 MV/cm the responses are $d_p = 13$ pC/N and $\kappa = 3.1$ nC/cm^{2}K. A charge meter malfunction prevented us from obtaining a polarization value on this sample.

There is considerable interest in apparent morphological changes during the poling process. (See for example, references 1 and 8.) From reflection x-ray diffractometer measurements on biaxially drawn PVDF (comprising both α and β phases), we have observed changes in structure at discrete intervals during the poling process. Fig. 5 shows the diffraction intensities with angle 2θ before and after poling at 3.4 MV/cm. Note that the (100), (020) and (120) reflections from the α phase essentially disappear after poling, whereas the (110) of α and the combined (110) and (200) of β appear to increase slightly. At this time it is not clear if these increases are significant. At 36° 2θ some changes occur, but, unfortunately, it is not possible to distinguish between contributions from α and β phases in this region.

When the same specimens are examined in transmission using photographic techniques, the (100) and (020) reflections are still readily apparent so that only certain crystal orientations with respect to poling field are affected in this manner.

In looking at the undrawn (α phase) sample, the situation appears to be slightly different, as revealed by Fig. 6. The (110), (020), and (100) intensities seem to diminish slightly with poling; however, none of these disappear as with the (020) and (100) for the biaxially stretched sample. The important result is that an additional reflection seems to appear at 20.7°, which would coincide with the (110) and (200) of β phase shown on Fig. 5. Based on this evidence alone, one might speculate that there is a partial conversion from α to β phase during poling. However, we have not observed any of the other reflections to be expected from β phase either by reflection in the diffractometer, by transmission in a flat plate camera or in a powder camera. The spacings obtained by us using the powder camera for the unpoled samples are in good agreement with those obtained in Refs. 11 and 12.

Our tentative conclusion is that the non-polar α phase is modified under the influence of high electric fields to yield a polar crystal phase which persists after removal of the external field. The unit cell of the α phase is non-polar but the TGTG' configuration within a given chain traverse of the crystal has a large component of dipole moment normal to the chain axis. The mechanism proposed would involve rotation of polymer chains about their own axes to align the dipole with the applied field resulting in a metastable state. Those crystallites oriented with the chain axis parallel to the surface of the film would be subjected to the largest interaction energy. It is clear that the applied field has altered the orientation of crystallites and perhaps the crystal structure, but the details are not yet resolved.

References

1. P. D. Southgate, Appl. Phys. Letters., 28, 250 (1976).

2. F. I. Mopsik and M. G. Broadhurst, J. Appl. Phys., 46, 4204 (1975).

3. M. G. Broadhurst, G. T. Davis, S. C. Roth, and R. E. Collins, Conference on Electrical Insulation and Dielectric Phenomena, Buck Hill Falls, Pa., October 1976.

4. Y. Wada and R. Hayakawa, Jap. J. Appl. Phys., 15, 2041 (1976).

5. M. G. Broadhurst, C. G. Malmberg, F. I. Mopsik, and W. P. Harris, in Electrets, Charge Storage and Transport in Dielectrics, M.M. Perlman, ed. Electrochem. Soc. Princeton, N.J., p.492 (1973).

6. K. Nakagawa and Y. Ishida, Kolloid Z. u. Z. Polymere, 251, 103 (1973).

7. W. W. Doll and J. B. Lando, J. Macromol. Sci.-Phys., B2, 219 (1968).

8. D. K. Das Gupta and K. Doughty, Appl. Phys. Letters, 31, 585 (1977).

9. H. Kakutani, J. Polym. Sci., A-2, 8, 1177 (1970).

10. M. G. Broadhurst and F. I. Mopsik, J. Chem. Phys., 52, 3634 (1970).

11. R. Hasegawa, Y. Takahashi, Y. Chatani, and H. Tadakoro, Polym. J., 3, 600 (1972).

12. W. W. Doll and J. B. Lando, J. Macromol. Sci., B-4, 309 (1970).

Table I
Experimental Values in SI Units of Quantities Appearing in Eqs. (5)

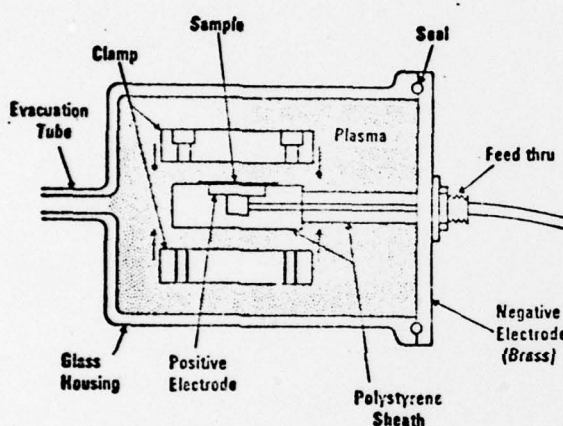| Quantity	Value	Reference
α_c	1.69×10^{-4}	6
β_c	1.56×10^{-10}	6,7
ε_c	3	9
ν	4.55	10
ϕ	0.284	2
T	300	-

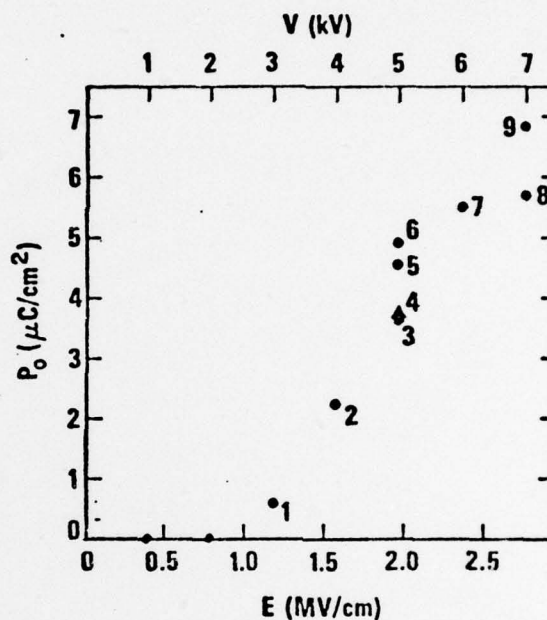FIGURE 1: Schematic drawing of poling electrode assembly.

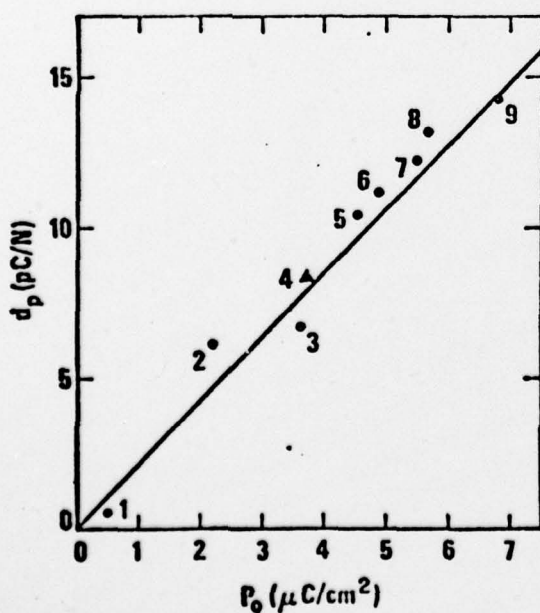FIGURE 2: Initial polarization versus applied field (or voltage) for bi-axially drawn PVDF.

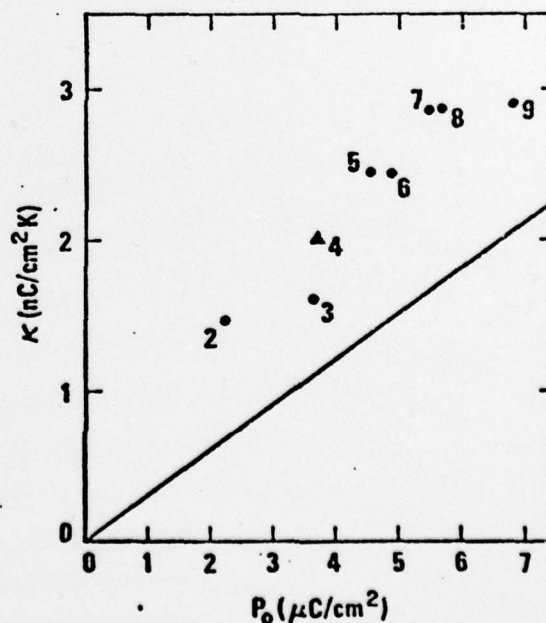FIGURE 3: Piezoelectric coefficient d_p versus initial polarization for biaxially drawn PVDF.

FIGURE 4: Pyroelectric coefficient κ versus initial polarization for biaxially drawn PVDF.
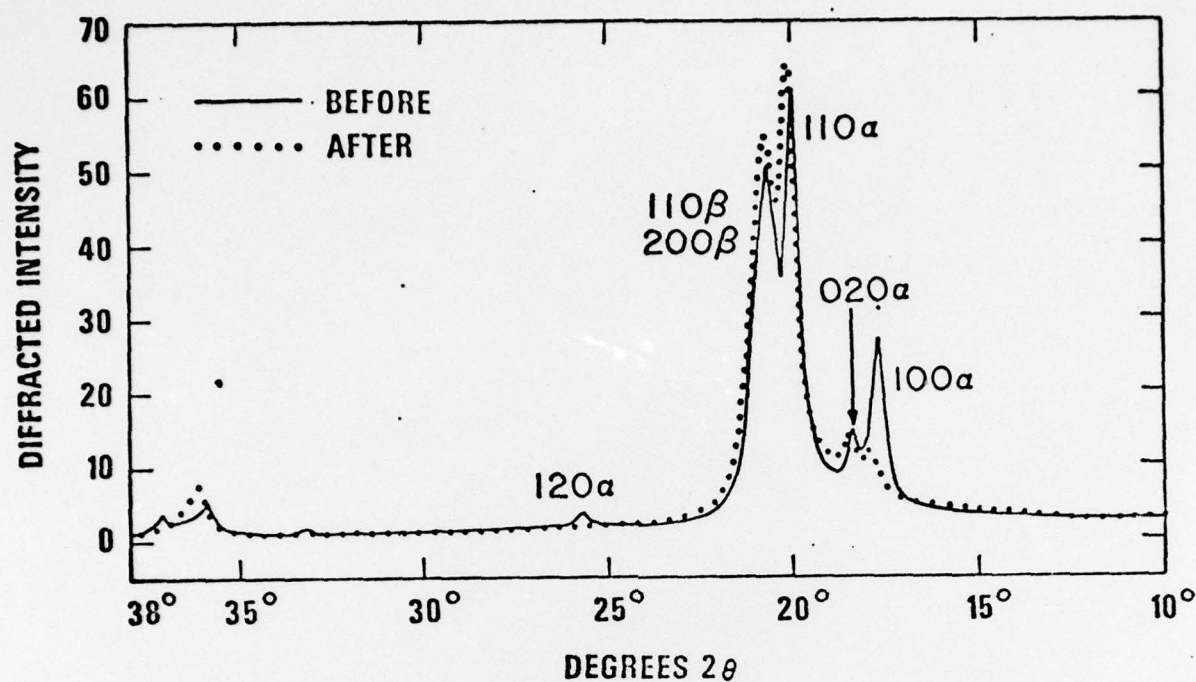
FIGURE 5. X-ray diffractometer scan for biaxially drawn
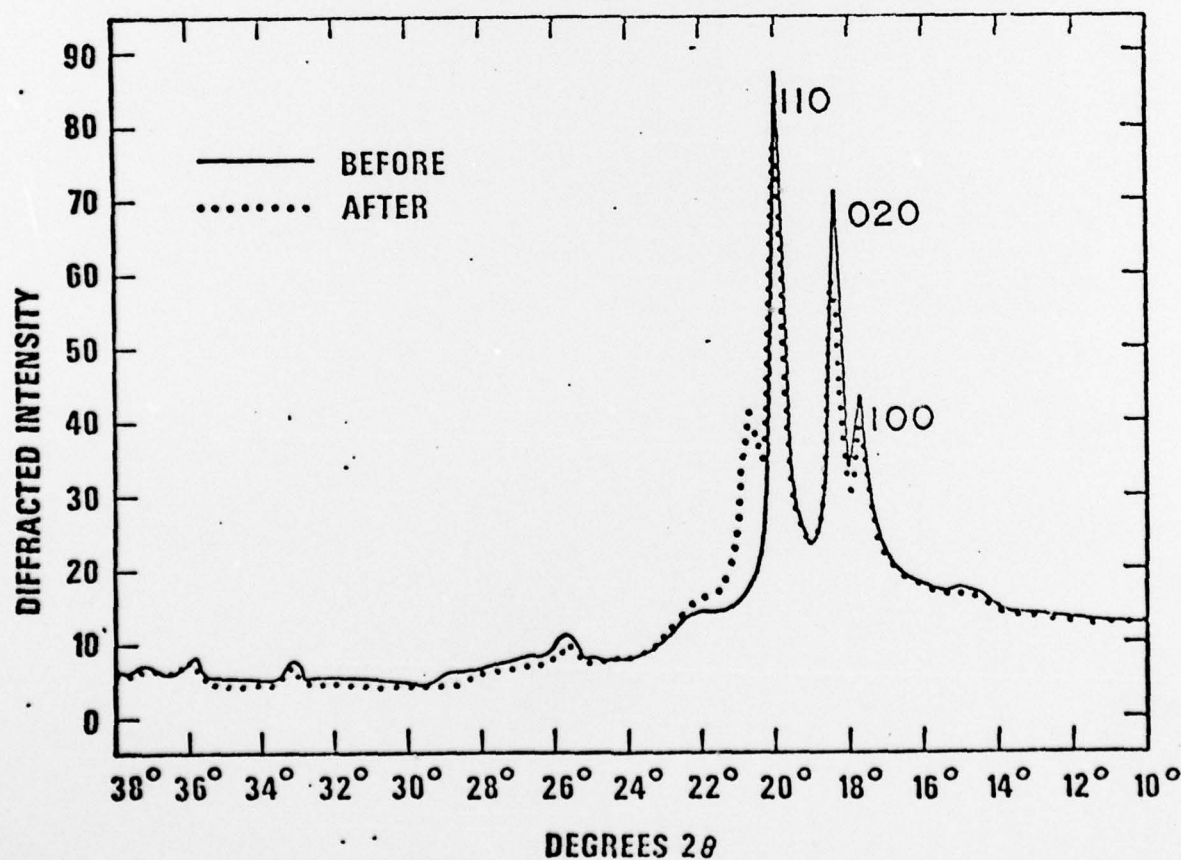PVDF before (——) and after (...) poling at 3.4 MV/cm.

FIGURE 6. X-ray diffractometer scan for undrawn PVDF
before (——) and after (...) poling at 1.7 MV/cm.

No. Copies   No. Copies

Dr. Stephen H. Carr
Department of Materials Science
Northwestern University
Evanston, Illinois 60201   1

Dr. M. Broadhurst
Bulk Properties Section
National Bureau of Standards
U.S. Department of Commerce
Washington, D.C. 20234   2

Dr. C. H. Wang
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112   1

Dr. T. A. Litovitz
Department of Physics
Catholic University of America
Washington, D.C. 20017   1

Dr. R. V. Submaranian
Washington State University
Department of Materials Science
Pullman, Washington 99103   1

Dr. M. Shen
Department of Chemical Engineering
University of California
Berkeley, California 94720   1

Dr. R. S. Porter
Polymer Research Institute and
Polymer Science and Engineering
University of Massachusetts
Amherst, Massachusetts 01002   1

Dr. Morton Litt   1
Dept. of Macromolecular Science
Case Western Reserve University
Cleveland, Ohio 44106

Dr. V. Stannett
Department of Chemical Engineering
North Carolina State University
Raleigh, North Carolina 27607 1

Dr. D. R. Uhlman
Department of Metallurgy and Material Science
Center for Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139   1

Naval Surface Weapons Center
White Oak
Silver Spring, Maryland 20910   1
Attn: Dr. J. M. Augl
       Dr. B. Hartmann

Dr. G. Goodman
Globe Union Inc.
5757 North Green Bay Avenue
Milwaukee, Wisconsin 53201   1

Picatinny Arsenal
SMUPA-FR-M-D
Dover, New Jersey 07801
Attn: A. M. Anzalone   1
       Bldg. 3401

Dr. J. K. Gillham
Princeton University
Department of Chemistry
Princeton, New Jersey 08540   1

Douglas Aircraft Co.
3855 Lakewood Boulevard
Long Beach, California 90846
Attn: Technical Library
       C1 290/36-84
       AUTO-Sutton   1

Dr. E. Baer
Department of Macromolecular Science
Case Western Reserve University
Cleveland, Ohio 44106   1

Dr. K. D. Pae
Department of Mechanics and Materials Science
Rutgers University
New Brunswick, New Jersey 08903   1

TECHNICAL REPORT DISTRIBUTION LIST

Office of Naval Research
Arlington, Virginia 22217
Attn: Code 472   2

Office of Naval Research
Arlington, Virginia 22217
Attn: Code 102IP   6

ONR Branch Office
536 S. Clark Street
Chicago, Illinois 60605
Attn: Dr. George Sandoz   1

ONR Branch Office
715 Broadway
New York, New York 10003
Attn: Scientific Dept.   1

ONR Branch Office
1030 East Green Street
Pasadena, California 91106
Attn: Dr. R. J. Marcus   1

ONR Branch Office
760 Market Street, Rm. 447
San Francisco, California 94102
Attn: Dr. P. A. Miller   1

ONR Branch Office
495 Summer Street
Boston, Massachusetts 02210
Attn: Dr. L. H. Peebles   1

Director, Naval Research Laboratory
Washington, D.C. 20390
Attn: Library, Code 2029 (ONRL)   6
       Technical Info. Div.   1
       Code 6100, 6170   1

The Asst. Secretary of the Navy (R&D)
Department of the Navy
Room 4E736, Pentagon
Washington, D.C. 20350   1

Commander, Naval Air Systems Command
Department of the Navy
Washington, D.C. 20360
Attn: Code 310C (H. Rosenwasser)   1

Defense Documentation Center
Building 5, Cameron Station
Alexandria, Virginia 22314   12

U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, North Carolina 27709
Attn: CRD-AA-IP

Commander
Naval Undersea Research & Development
Center
San Diego, California 92132
Attn: Technical Library, Code 133   1

Naval Weapons Center
China Lake, California 93555
Attn: Head, Chemistry Division   1

Naval Civil Engineering Laboratory
Port Hueneme, California 93041
Attn: Mr. W. S. Haynes   1

Professor O. Heinz
Department of Physics & Chemistry
Naval Postgraduate School
Monterey, California 93940

Dr. A. L. Slafkosky
Scientific Advisor
Commandant of the Marine Corps (Code RD-1)
Washington, D.C. 20380   1

NASA-Lewis Research Center
21000 Brookpark Road
Cleveland, Ohio 44135
Attn: Dr. T. T. Serofini, MS-49-1 1

Dr. Charles H. Sherman, Code TD 121
Naval Underwater Systems Center
New London, Connecticut   1

Dr. William Risen
Department of Chemistry
Brown University
Providence, Rhode Island 02912   1

Dr. Alan Gent
Department of Physics
University of Akron
Akron, Ohio 44304   1

Mr. Robert W. Jones
Advanced Projects Manager
Hughes Aircraft Company
Mail Station D 132
Culver City, California 90230   1

Dr. C. Giori
IIT Research Institute
10 West 35 Street
Chicago, Illinois 60616   1

Dr. Jerome B. Lando   1
Dept. of Macromolecular Science
Case Western Reserve University
Cleveland, Ohio 44106

Dr. David Roylance
Department of Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02039   1

Dr. W. A. Spitzig
United States Steel Corporation
Research Laboratory
Monroeville, Pennsylvania 15146   1

Dr. T. P. Conlon, Jr., Code 3622
Sandia Laboratories
Sandia Corporation
Albuquerque, New Mexico 87115   1

Dr. Martin Kaufmann, Head
Materials Research Branch, Code 4542
Naval Weapons Center
China Lake, California 93555   1

Dr. Charles Hicks
Naval Undersea Center
San Diego, California 92132
                                   1

Mr. A. Johnson N43-12
National Highway Traffic Safety Admin. 1
2100 2nd Street, S.W.
Washington, D.C. 20590

2